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**SURFACE ACOUSTIC WAVE DETECTION OF
ORGANOPHOSPHORUS COMPOUNDS**

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<p>Surface Acoustic Wave (SAW) devices are potentially useful as small, sensitive chemical vapor sensors. The operating principles of these devices have been described in detail. Their use in detecting dimethyl methylphosphonate vapor has been reported previously. The basic operating principle for the SAW devices is the reversible adsorption of chemical vapors by adsorbent coatings that are sensitive and selective to the vapors that one is trying to detect. That is, SAW devices act as mass sensitive detectors. The SAW device used in this study consists of an array of four coated sensor elements with each coating giving a characteristic response to each of the vapors to be detected. The coatings used for the four sensors are fluoropolyol (FPOL), poly(ethylene maleate) (PEM), ethyl cellulose (ECEL), and polyvinyl pyrrolidone (PVP). The chemical vapors detected were diethyl ethylphosphonate (DEEP), dimethyl methylphosphonate (DMMP), (continued on reverse)</p>					
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diisopropyl methylphosphonate (DIMP), and dimethyl hydrogenphosphonate (DMHP). These vapors were chosen because they are all organophosphonates and would give the responses of the sensors as a function of molecular weight as well as a function of the concentration of the vapors. This hypothesis assumes that the solubilities of the organophosphorus compounds are similar for a specific coating.

PREFACE

The work described in this report was authorized under Project No. 1C464724D020, Chemical Detection and Warning Systems. This work was started in May 1987 and completed in October 1987.

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This report has been approved for release to the public.

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SURFACE ACOUSTIC WAVE DETECTION OF ORGANOPHOSPHORUS COMPOUNDS

1. INTRODUCTION

Surface Acoustic Wave (SAW) devices are potentially useful as small, sensitive chemical vapor sensors. The operating principles of these devices have been described in detail,* and their use in detecting dimethyl methylphosphonate vapor has been reported previously.** The basic operating principle for the SAW devices is the reversible adsorption of chemical vapors by adsorbent coatings that are sensitive and selective to the vapor that one is trying to detect. That is, SAW devices act as mass sensitive detectors. The SAW device used in this study consists of an array of four coated sensor elements with each coating giving a characteristic response to each of the vapors to be detected. The coatings used for the four sensors are fluoropolyol (FPOL), poly(ethylene maleate) (PEM), ethyl cellulose (ECEL), and polyvinyl pyrrolidone (PVP). The chemical vapors detected were diethyl ethylphosphonate (DEEP), dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), and dimethyl hydrogenphosphonate (DMHP). These vapors were chosen because they are all organophosphonates and would give the responses of the sensors as a function of molecular weight as well as a function of the concentration of the vapors. This hypothesis assumes that the solubilities of the organophosphorus compounds are similar for a specific coating.

2. THEORY

Each of the SAW sensors used in this study consists of a pair of interdigital electrode arrays that are lithographically patterned on a polished piezoelectric material (e.g., ST-quartz). When placed in an oscillation circuit, an acoustic Rayleigh wave may be generated by applying an RF voltage to one set of the interdigital arrays. The generated Rayleigh wave travels across the quartz surface until it reaches the opposite set of electrodes. Most of the energy is constrained to the surface of the piezoelectric material. The Rayleigh wave will interact with any material that is in contact with the surface (i.e., the coating). Any changes in the mass or mechanical

* Snow, A., and Wohltjen, H., "Poly(ethylene maleate)-Cyclopentadiene: A Model Polymer-Vapor System for Evaluation of a SAW Microsensor," Anal. Chem. Vol. 56(8), p 1411 (1984).

** Miller, R.E., and Parsons, J.A., "Detection of Dimethyl Methylphosphonate Using a Surface Acoustic Wave Vapor Detector," Paper #40, presented at the American Chemical Society 21st Mid-Atlantic Regional Meeting, Pomona, NJ, 20 May 1987.

modulus of the coating will produce a change in the velocity of the Rayleigh wave, resulting in a measurable shift in the sensors resonant frequency. This study used dual-delay line oscillators that resonated at a frequency determined by the wave velocity and the electrode spacing. Using the delay line oscillators allowed for the compensation of any temperature and vapor flow rate variations experienced by the sensor. This is accomplished by comparing the resonant frequency of a wave propagating across a coated surface with a wave propagating across an uncoated surface. A schematic of the 158 Megahertz (MHz) dual-delay line oscillator used in this study is shown in Figure 1.

3. EXPERIMENTAL PROCEDURES

3.1 Equipment.

The equipment used in this study consists of a SAW vapor sensor that is interfaced to an Apple IIe computer (Figure 2) and a Q5 vapor generator (Figure 3). The SAW sensor, obtained from Dr. Hank Wohltjen (Microsensor Systems, Incorporated), incorporates four separate 158-MHz dual-delay line oscillators coated with FPOL, PEM, ECEL, and PVP. The materials used for the sensor coatings were provided by the Naval Research Laboratory (Washington, DC) and Microsensor Systems, Incorporated. The chemical structures of the coatings are shown in Table 1.

The coatings were applied to packaged, wire-bonded bare oscillators using a standard air brush with compressed air as the propellant and solutions of the coatings dissolved in volatile solvents. Typical solutions for the air brush procedure are 0.1 wt % coating in chloroform. The wire-bonded bare oscillator is composed of two sets of interdigital electrodes consisting of 50 gold-plated "fingers." The fingers are 7- μ m wide, and the spacing between fingers measures 7 μ m. The fingers were lithographically patterned onto ST-Quartz, a substrate material. The entire package was then placed into a Teflon cell for use. The total area of the dual-delay line oscillator is approximately 1 cm² (1 cm by 1 cm²). Because the area of the oscillator to be coated measured about 2 mm², a mask was placed over the oscillator to ensure proper deposition of the coatings. The film thickness was determined by measuring the frequency change of the oscillator's resonant frequency during the coating application with the frequency change being monitored by an oscilloscope. The coatings were applied to the wire-bonded bare oscillators by the staff at Naval Research Laboratory.

The low concentrations of the sample vapors were generated with a standard Q5 generator by passing dry zero air, at a known flow rate, through a porous alundum oxide thimble saturated with the liquid reagent. The porous thimble and the

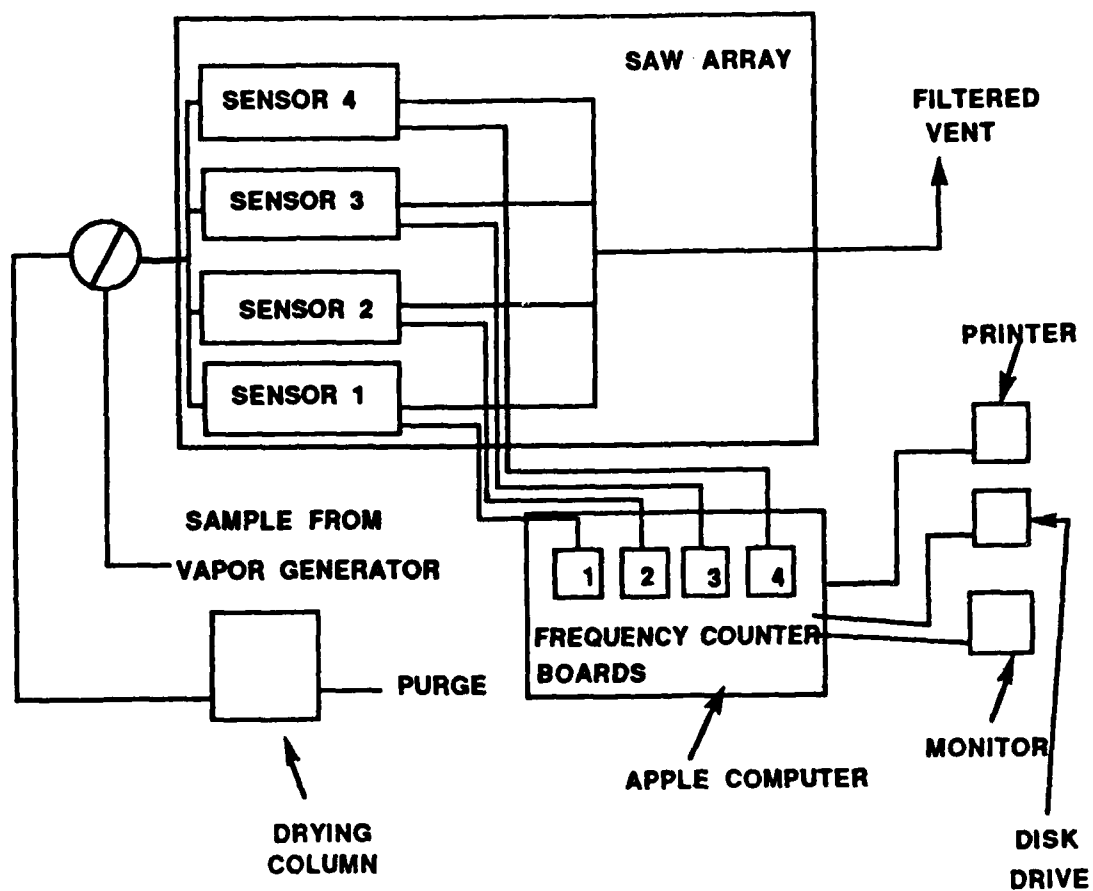


Figure 1. Block Diagram of the SAW Equipment.

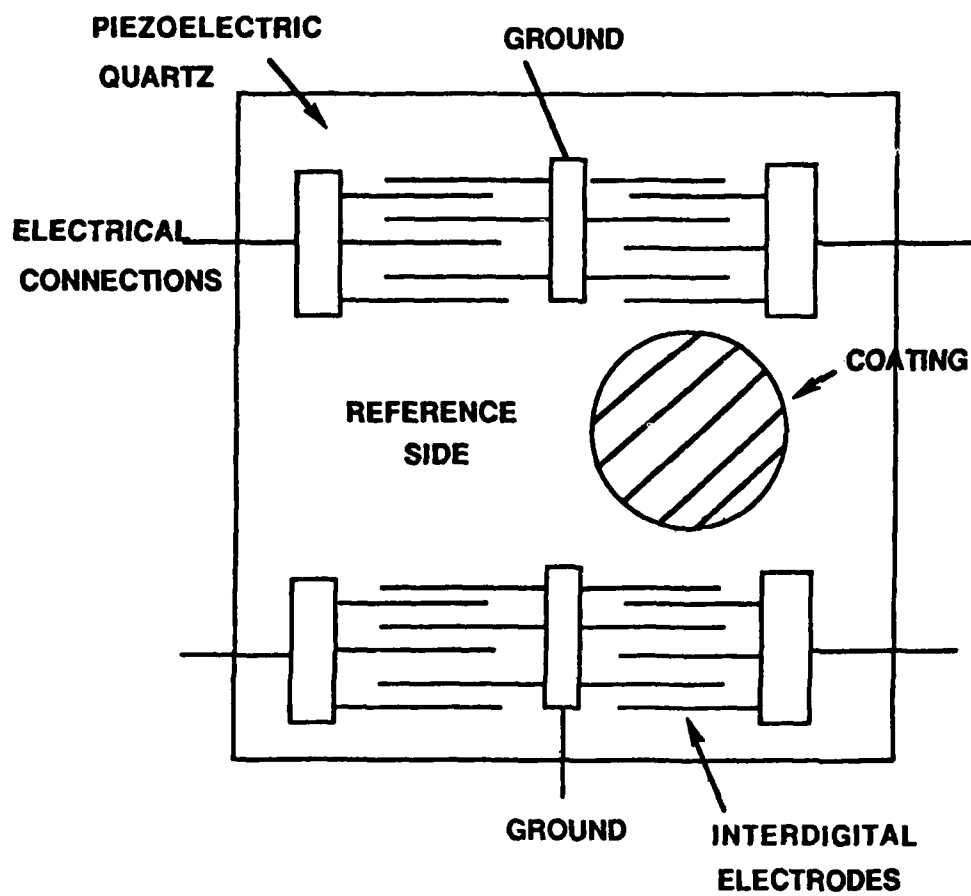


Figure 2. 158 MHz Dual Delay Line Oscillator.

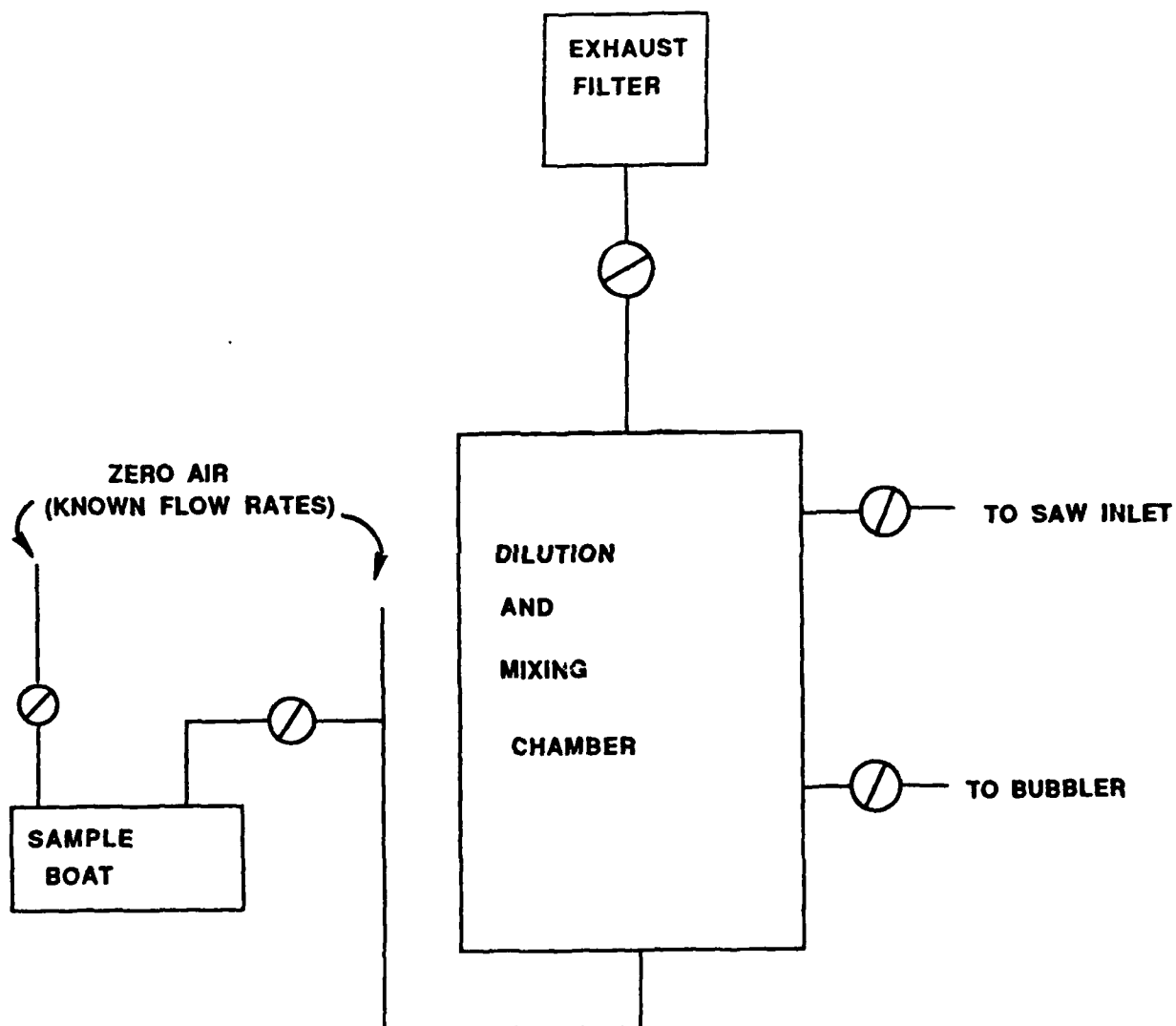
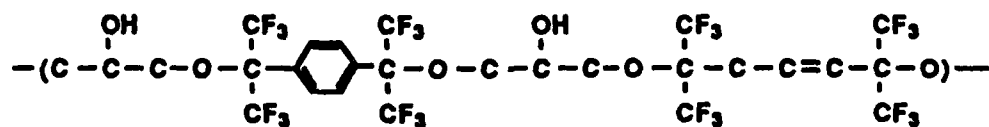
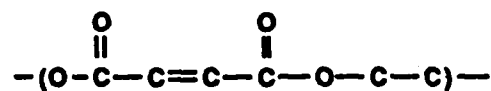


Figure 3. Diagram of a Q5 Vapor Generator.

Table 1. Chemical Structures of the Coatings.



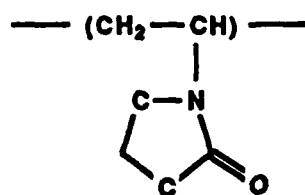
Fluoropolyol



Poly(ethylene maleate)



Ethyl Cellulose



Polyvinyl Pyrrolidone

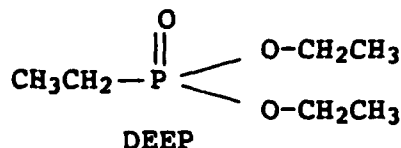
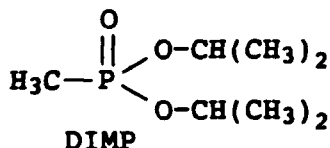
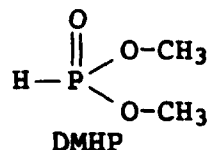
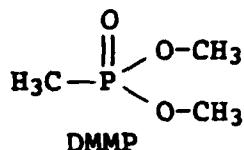
liquid reagent are both contained within a sample boat. This vapor is then mixed and diluted to the desired concentration with dry zero air in the generator's mixing chamber where the flow and concentration of the vapor are allowed to stabilize. Two sampling ports on the generator mixing chamber provide access to the sample vapor. One of the ports permits sampling of the vapor by the SAW device during its sampling cycle. The second port permits samples of the vapor to be removed for analysis. This second sample is removed by bubbling the vapor, at a known flow rate and sample collection time, through a set of two bubblers each filled with 10 mL of either 2-methoxy-ethanol or isopropyl alcohol. The bubblers are then analyzed using gas chromatography (GC). The first sampling port leads to a three-way, manually operated switching valve that allows the SAW device to sample the generated vapor or a purge of zero air. Typically, the SAW samples the zero air purge for 2 min to establish an initial baseline. Then the switching valve is positioned to allow sampling of the vapor for approximately 2-5 min or until an equilibrium frequency shift is observed. The switching valve is repositioned to allow sampling of the zero air purge, and the SAW establishes a final baseline.

The GC analysis was conducted on a Model 5880A Hewlett-Packard GC. The GC was equipped with a flame photometric detector (FPD) operated at 220 °C. The injection temperature of the GC was set to 250 °C. The column used for the analysis was a 6 ft by 0.2-mm column with 4.61% OV-101 and 3.39% OV-17 on a stationary phase of 100-120 Gaschrome Q. The sample size injected into the GC was 2 µL with a nitrogen flow rate of 30 mL/min. Temperature programming of the oven in the 60-250 °C range was used. The concentrations of the vapors in the bubblers were based on peak area measurements and external standards. Peak tailing was generally observed for the samples. The concentration of the vapor in the Q5 generator was then calculated from the concentration of the bubbler using the time collection of the bubbler, flowrate of the sample through the bubbler, and the molecular weight of the sample.

3.2 Chemicals.

The organophosphorus compounds used in this study were DMHP (83% pure), DIMP (95% pure), and DEEP (97% pure) all obtained from the Aldrich Chemical Company (Milwaukee, WI), and DMMP (98% pure) obtained from the Stauffer Chemical Company (Westport, CT). The purity of these compounds was determined using NMR analysis, and the structures of these compounds are shown in Table 2.

Table 2. Structures of the Organophosphorus Compounds.



4. DISCUSSION AND RESULTS

Tables 3 through 6 contain the raw data for the responses of the coatings to the four vapor challenges. Figures 4 through 7 show typical response curves obtained for nominal 10-parts-per-million (ppm) concentrations of the test vapors for the four coatings. The responses reported in the tables are average values for the responses based on repeated exposures for each concentration run. Figures 8 through 11 are graphs of the frequency shift of the coatings corrected for coating thickness (in hertz/kilohertz coating) versus concentration of the vapors (ppm) of the coatings studied, the largest frequency shifts observed were for the FPOL coating with the next larger response being obtained for the PEM. For ECEL and PVP, there is generally a very small response. The frequency shifts for the sensors are the differences between equilibrium frequency readings of the sensor with the sample present in the SAW and the average of the baseline frequency reading of the sensor before the sample is introduced to the SAW and after the sample has been removed from the SAW.

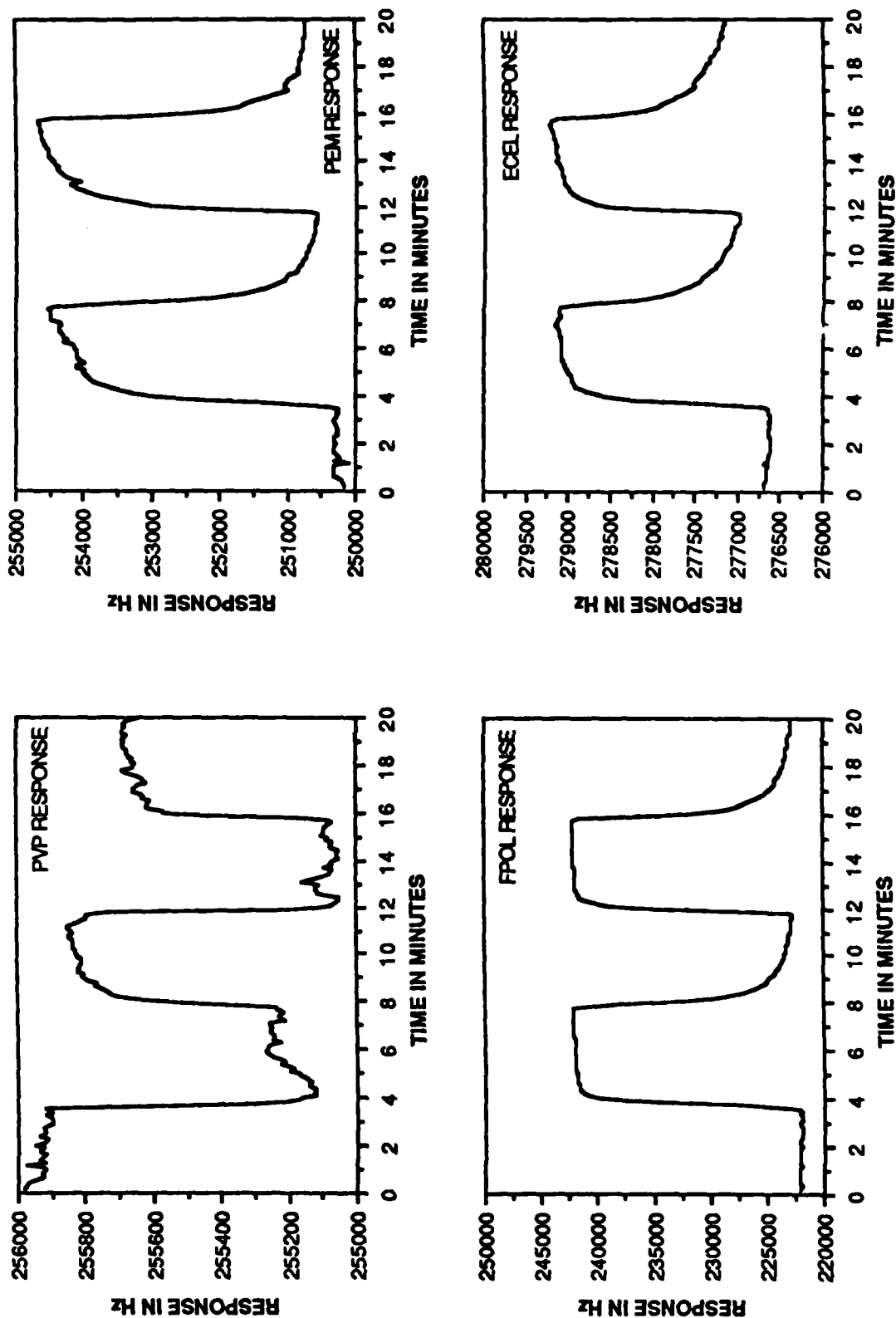


Figure 4. Typical SAW Responses to Nominal 10 ppm DMMP Vapor.

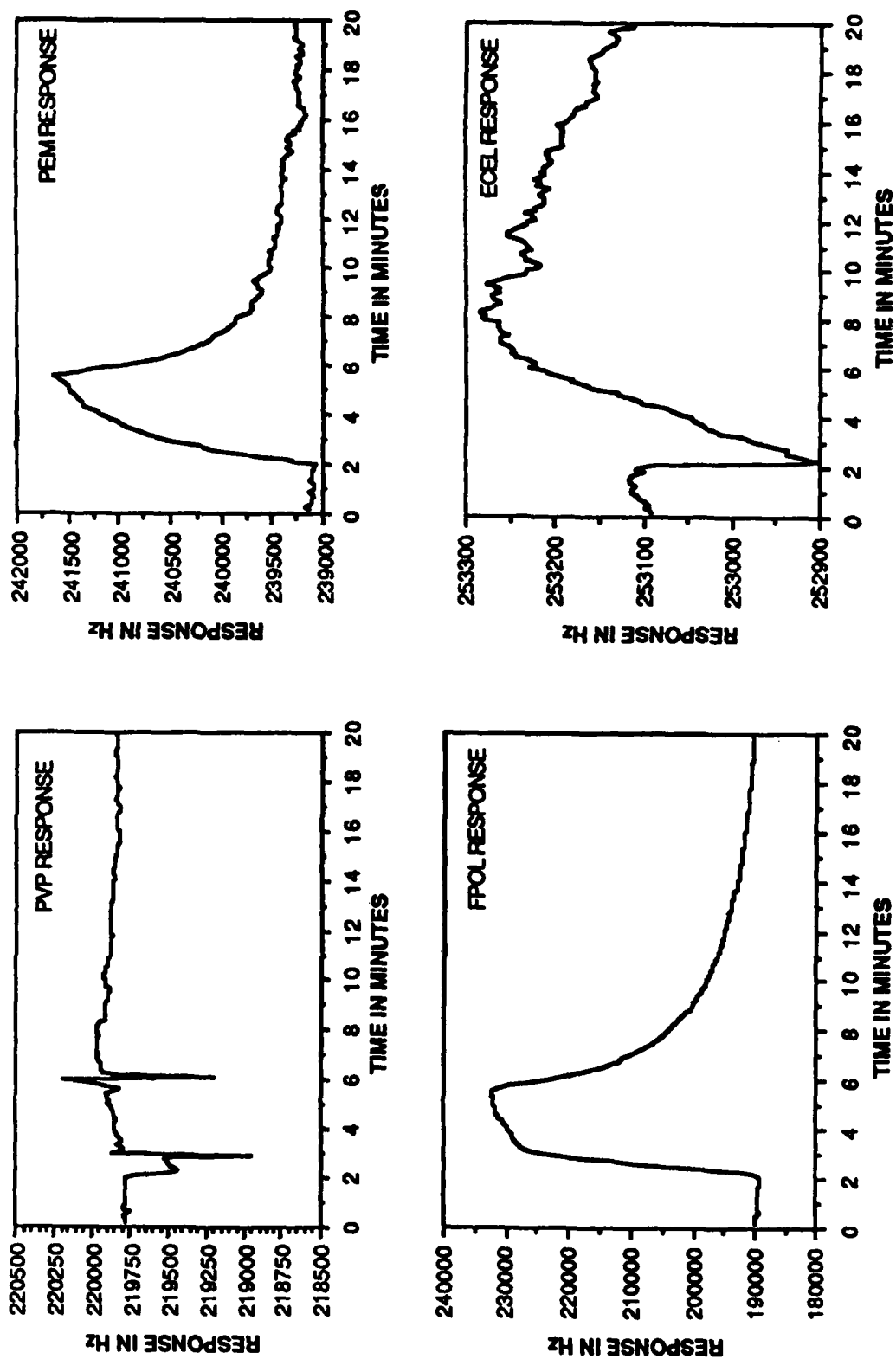


Figure 5. Typical SAW Responses to Nominal 10 ppm DIMP Vapor.

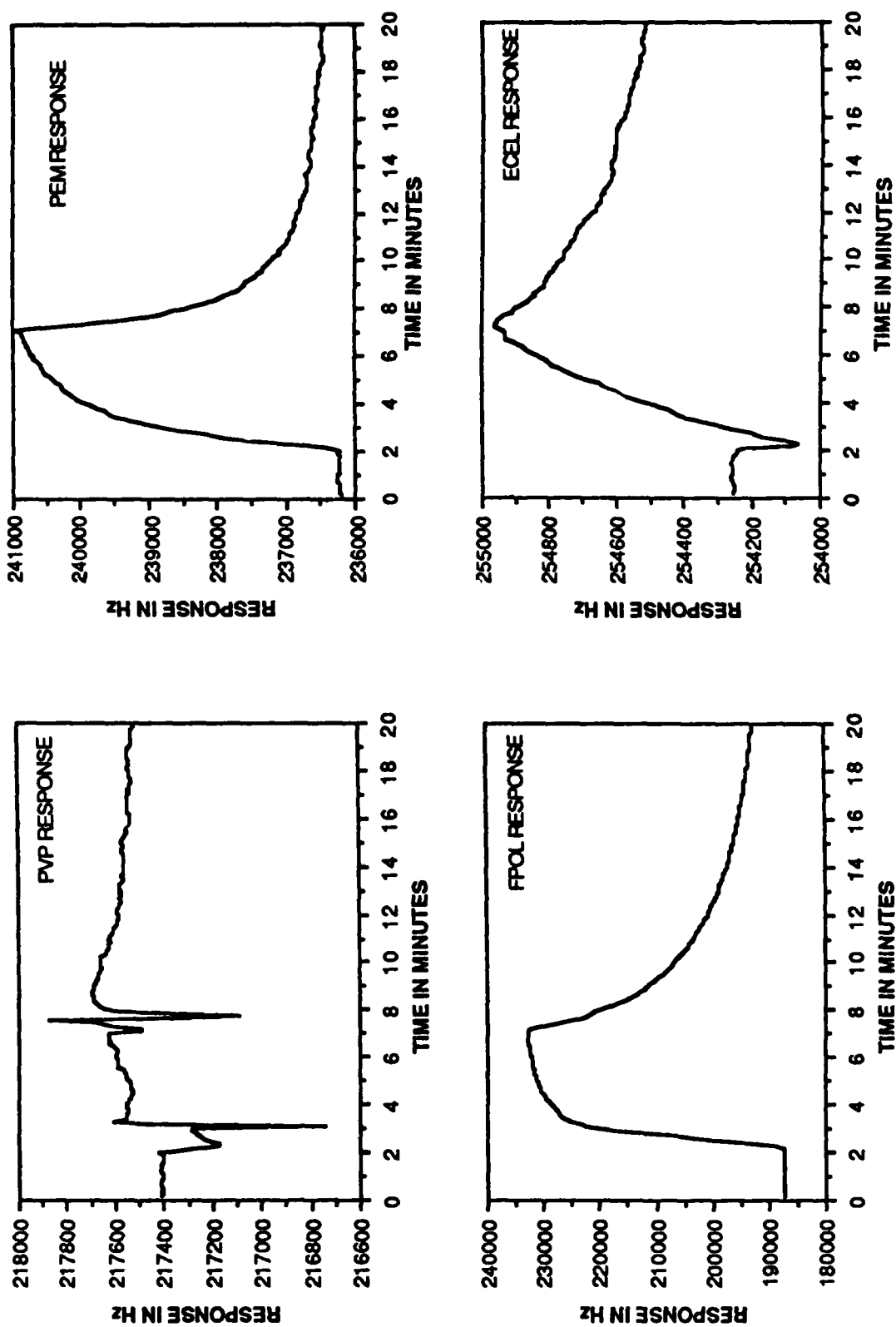


Figure 6. Typical SAW Responses to Nominal 10 ppm DEEP Vapor.

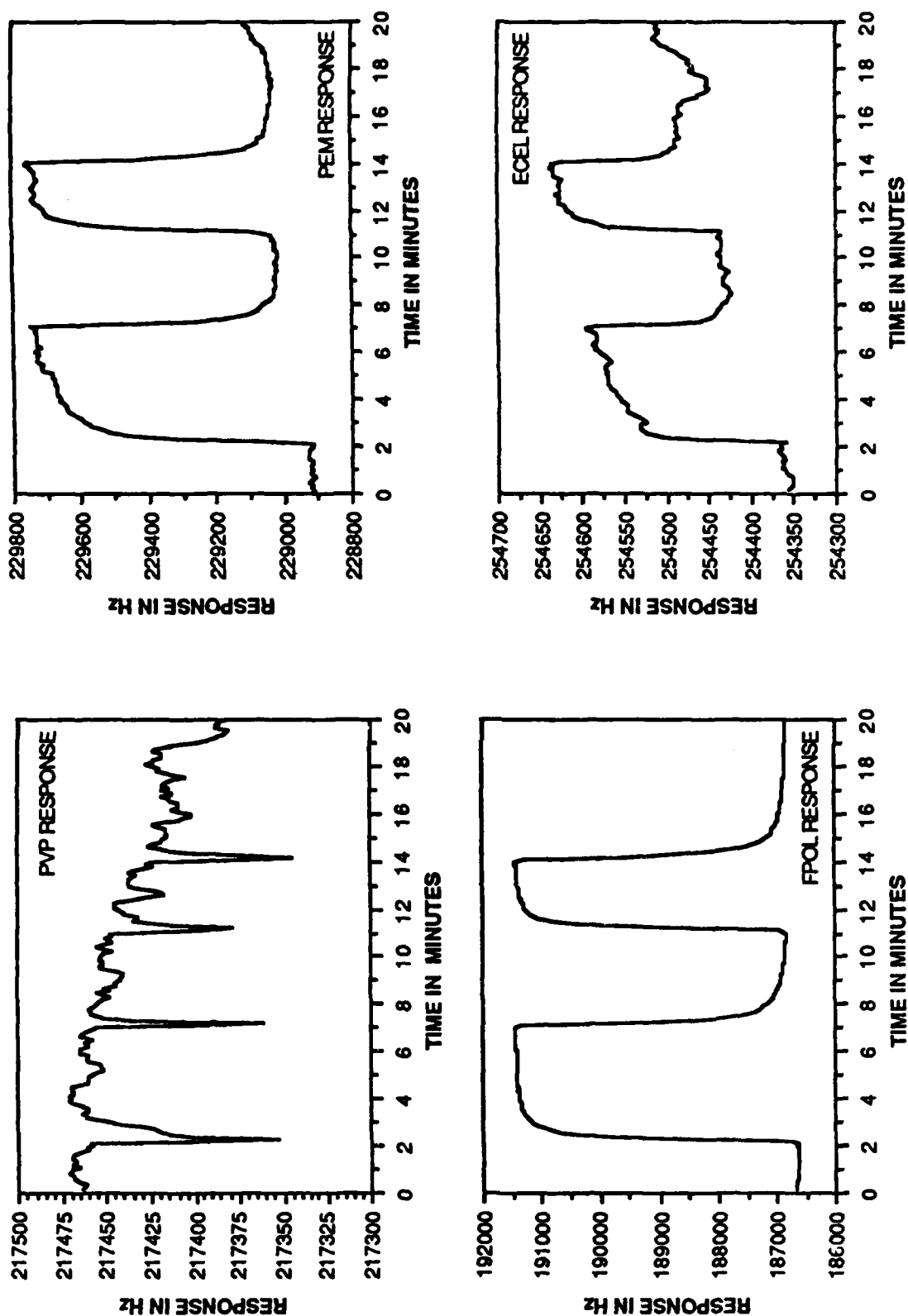


Figure 7. Typical SAW Responses to Nominal 10 ppm DMHP Vapor.

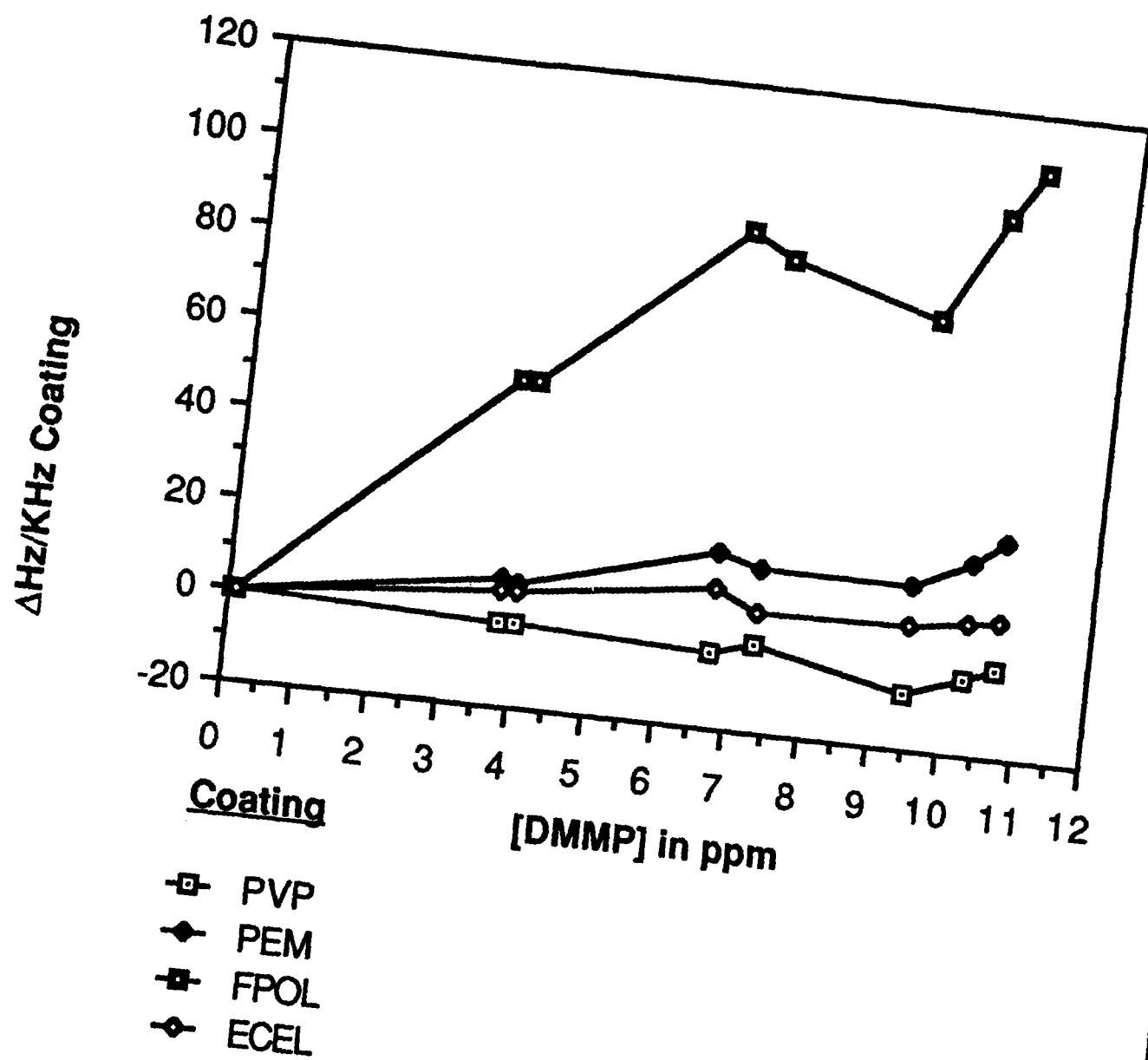


Figure 8. SAW Response to DMMP Vapor.

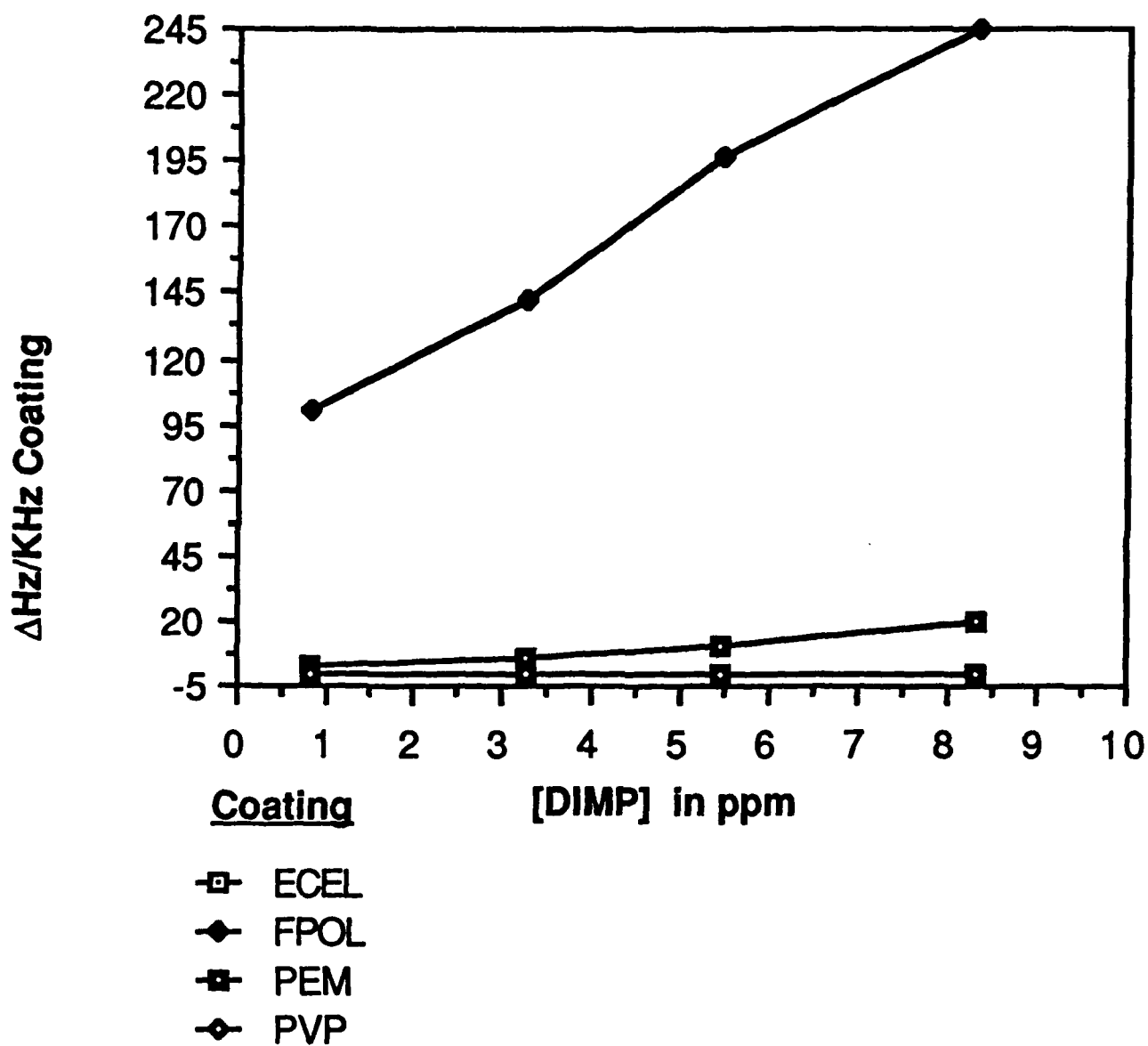


Figure 9. SAW Response to DIMP Vapor.

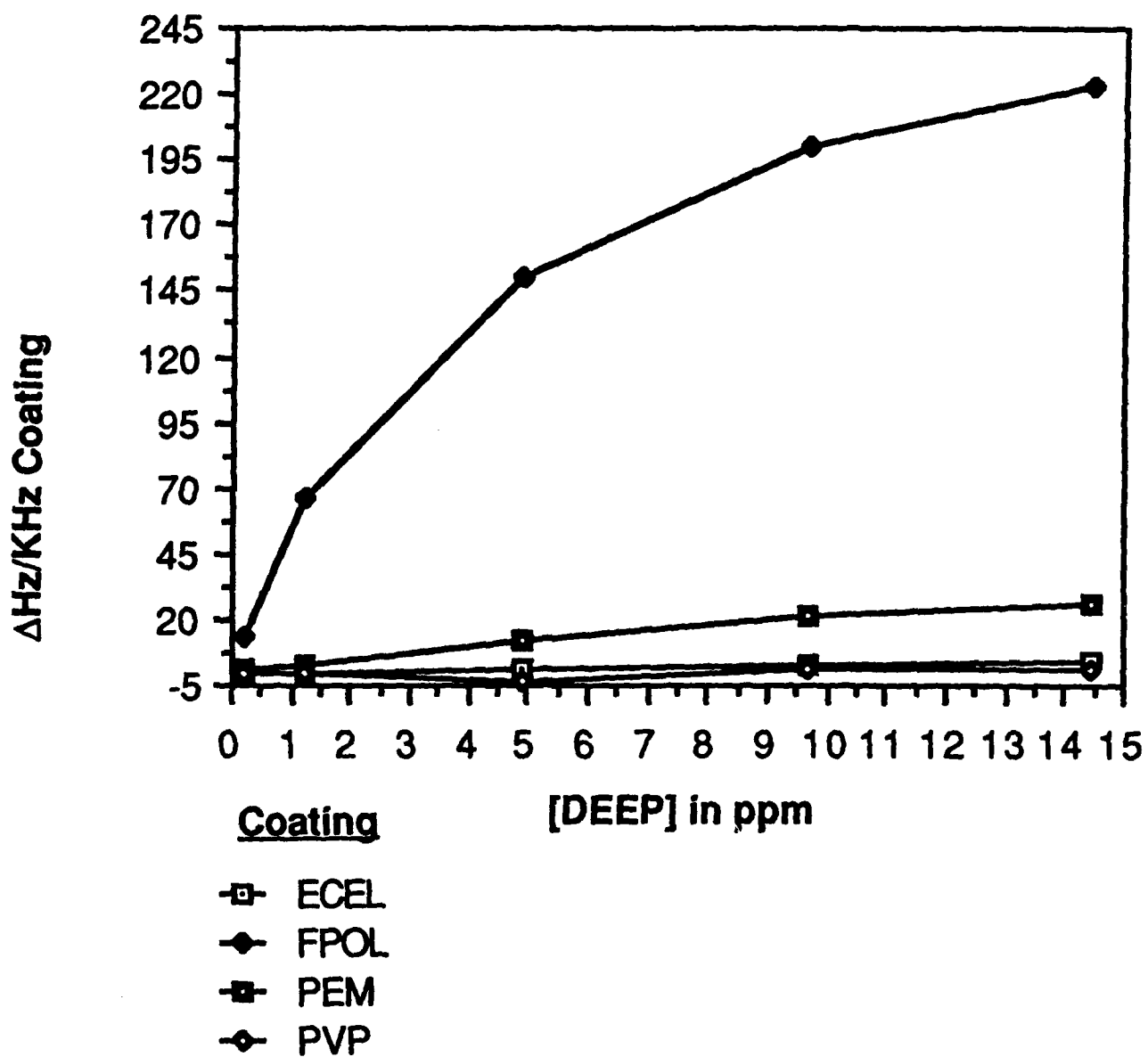


Figure 10. SAW Response to DEEP Vapor.

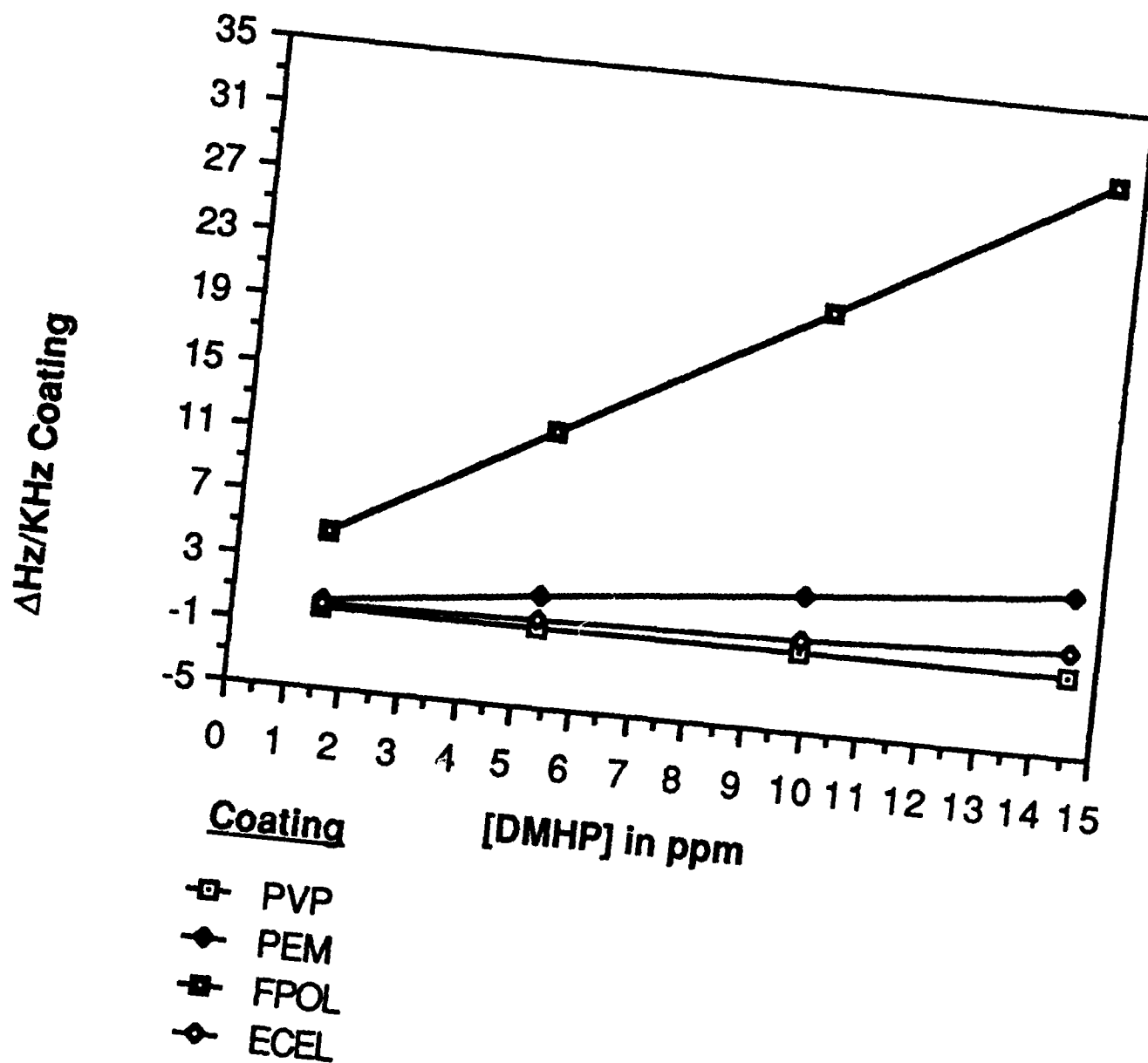


Figure 11. SAW Response to DMHP Vapor.

4.1 Response to DMMP.

The frequency shifts of the four sensor coatings to DMMP vapor is shown in Table 3. The frequency shift for Table 3 is the average frequency shift obtained for the sensor response. In general, the average is for four different runs with two exposures of the sensor to the vapor per run. Table 3 shows that FPOL has the largest response (i.e., frequency shift) for the DMMP vapor with PEM exhibiting the next greater response. Generally, the ECEL response is greater than the response obtained using the PVP. The PVP is the only sensor used in this study that exhibited a negative frequency shift when the DMMP vapor was introduced into the SAW.

Table 3. SAW Response to DMMP Vapor.

DMMP Concentration (ppm)	Frequency Shift (Δ Hz) for Sensor			
	FPOL	PEM	ECEL	PVP
0.033	36 \pm 12	15 \pm 7	45 \pm 58	18 \pm 15
0.044	46 \pm 10	4 \pm 9	-2 \pm 11	-2 \pm 14
0.086	89 \pm 36	12 \pm 17	5 \pm 32	-23 \pm 29
0.105	19 \pm 7	11 \pm 5	9 \pm 17	17 \pm 18
3.77	11219 \pm 94	1781 \pm 26	1137 \pm 109	-420 \pm 139
4.00	11337 \pm 132	1542 \pm 33	1014 \pm 106	-403 \pm 145
6.72	19430 \pm 183	3934 \pm 54	2128 \pm 122	-674 \pm 30
7.33	18284 \pm 395	3437 \pm 150	1199 \pm 103	-154 \pm 139
9.44	16289 \pm 183	3514 \pm 51	1382 \pm 273	-1613 \pm 228
10.23	21418 \pm 845	4759 \pm 245	1703 \pm 322	-769 \pm 323
10.71	23718 \pm 344	5999 \pm 57	1948 \pm 281	-130 \pm 231

The interactions between the DMMP and the sensor coatings all seem reversible; but, the solubility or strength of interaction of the coatings with the vapor vary greatly. The interaction of the PVP with the DMMP is almost nonexistent; whereas, the interaction of the FPOL and PEM is much greater. This is evident from the relative intensities of the frequency shifts observed for the coatings. The interaction of the DMMP with the PVP is so small that it appears the ST-Quartz interaction with the vapor is much greater. This would explain why a negative frequency shift is observed for the PVP coating as any vapor adsorbed in the coating would result in a positive frequency shift. The only other explanation for the negative shift would be that the DMMP vapor is stripping the PVP coating off the oscillator. This does not appear to be happening because the sensor response returns to its baseline value when the DMMP vapor is removed from the SAW.

4.2 Response to DIMP.

The frequency shifts observed for the four sensor coatings when exposed to DIMP vapor are shown in Table 4. Note that the FPOL response is greater than the response obtained for PEM, PVP, or ECEL. Also note that the magnitude of the response obtained for the DIMP vapor is much greater for the FPOL coating than the response obtained for DMMP. The PEM response to the DIMP vapor is also generally less than the response obtained for the DMMP vapor. If the response were truly a function of the molecular weight, the DIMP response would be approximately 1.45 times greater than the response obtained for DMMP; 1.45:1 being the ratio of the molecular weights of the two compounds. The molecular weight of the DIMP is ~ 180 g/mole, and the molecular weight of the DMMP is ~ 124 g/mole. This ratio is not seen; in fact, the response observed for the DIMP is greater than 2 times that observed for the DMMP when the responses of the FPOL are compared. The response of the PEM is the reciprocal of that ratio at 5 ppm concentration. The ratio of the response of the PEM coating increases to approximately 1 at higher concentrations. Thus, it seems that the FPOL coating has a higher affinity for DIMP than it does for DMMP. The reverse is true for the PEM coating. But, the affinity of the PEM coating for the DIMP and DMMP approaches the same value as the concentration increases. This may be because the amount of vapor adsorbed in the coating approaches a saturation point.

Table 4. SAW Response To DIMP Vapor.

DIMP Concentration (ppm)	Frequency Shift (Δ Hz) for Sensor			
	FPOL	PEM	ECEL	PVP
0.803	22194 \pm 252	683 \pm 32	-130 \pm 40	27 \pm 58
3.29	31418 \pm 292	1134 \pm 73	-215 \pm 39	-81 \pm 74
5.44	43398 \pm 708	2319 \pm 57	-89 \pm 37	74 \pm 39
8.33	53751 \pm 920	4409 \pm 286	50 \pm 111	-69 \pm 59

The desired result would be for the SAW sensor responses to be linear with respect to concentration. This does not happen, even for the sensors that have small responses to the DIMP vapor. The PEM sensor is the closest there is to a linear response, whereas, the worst is the PVP response. Although not linear, the FPOL response does increase with an increase in the concentration of the vapor.

4.3 Response to DEEP Vapor.

The responses of the SAW coatings to DEEP vapor are shown in Table 5. The molecular weight of the DEEP is ~ 166 g/mole, so it would be expected that the SAW responses would lie between the response of the DIMP and that of the DMMP. The ratio of the responses of the sensors to the DMMP, DIMP, and DEEP would be expected to be 1:1.45:1.33, respectively. This relationship holds for the DIMP and DEEP at high concentrations (i.e., those concentrations above 5 ppm) for the FPOL coating; but, the ratio does not hold for the PEM coating at any concentration. The relationship does not fit at all for the DMMP to DEEP ratio for any sensor. The FPOL and PEM coatings seem to have a greater affinity for the DEEP vapor than they do for either the DIMP or DMMP vapors. This is evidenced by the slow return to baseline of the sensors after the vapor challenge has been removed. The affinity of the ECEL coating for the DMMP vapor is greater than its affinity for the DEEP vapor. The affinity of the coating for the DEEP vapor is greater than its affinity for the DIMP vapor. The response of the PVP coating is extremely erratic, and no trend has been noted for the vapors.

Table 5. SAW Response To DEEP Vapor.

DEEP Concentration (ppm)	Frequency Shift (Δ Hz) for Sensor			
	FPOL	PEM	ECEL	PVP
0.201	3099 \pm 379	173 \pm 94	-41 \pm 59	-9 \pm 50
1.22	14476 \pm 43	687 \pm 60	53 \pm 30	8 \pm 43
4.90	32973 \pm 487	2476 \pm 44	248 \pm 28	-721 \pm 10
9.7	44085 \pm 1054	4535 \pm 46	598 \pm 45	168 \pm 17
14.45	49198 \pm 743	5735 \pm 110	759 \pm 69	134 \pm 68

4.4 Response to DMHP Vapor.

The responses of the SAW sensor coatings to DMHP vapor are shown in Table 6. The molecular weight of the DMHP is ~ 110 g/mole, so it is the lightest of the organophosphorus compounds tested. If the responses of the coatings were strictly a function of the molecular weight, the ratio of the responses to DMMP, DIMP, DEEP, and DMHP would be 1:1.45:1.33:0.887, respectively. This relationship does not hold for any of the sensors tested at any concentration. Generally, the responses obtained for the DMHP vapor are an order of magnitude less than the responses obtained for any of the coatings. This means the affinities of the coatings to the DMHP vapor are much less than those for the other vapors. This may be because of the hydrogen that is attached to the

phosphorus atom in this molecule. All of the other vapors tested had either methyl or ethyl groups attached to the phosphorus. One result of the lower responses obtained for the DMHP vapor is that the responses of the FPOL and the PEM coatings are linear with respect to concentration. This linear response has not been obtained for any of the other vapors tested, and the linear response may be attributed to the low amount of DMHP vapor adsorbed by the coatings. This low adsorption of the DMHP vapor gives a greater concentration range of the vapor available for testing before saturation of the coating occurs.

Table 6. SAW Response to DMHP Vapor.

DMHP Concentration (ppm)	Frequency Shift (Δ Hz) for Sensor			
	FPOL	PEM	ECEL	PVP
1.56	1029 \pm 54	98 \pm 41	38 \pm 34	-1 \pm 10
5.3	2691 \pm 34	410 \pm 22	89 \pm 18	4 \pm 18
9.89	4632 \pm 48	734 \pm 27	157 \pm 21	16 \pm 15
14.5	6699 \pm 97	1097 \pm 47	276 \pm 15	-7 \pm 11

5. CONCLUSIONS

The data above show that the responses of the four coatings tested to the four vapors tested vary greatly. The PVP coating appears to be almost useless for detecting organophosphorus compounds because the coatings' response to the vapors is very small. The response is erratic when noted for the PVP. There is no semblance of a relationship of the response to the concentration of the vapor challenge. Making an approximation of the response of the coating to the molecular weight of the compound is also not possible because of the erratic nature of the response.

The ECEL coating has a much higher response to the organophosphorus vapors than the PVP coating does; but, ECEL's use as a sensor for organophosphorus compounds is limited. The response of the ECEL coating does not scale as a function of the molecular weight of the vapor. The ECEL coating responds as a function of the concentration of each vapor with the exception of the DIMP. ECEL's use as a sensor for the organophosphorus compounds is limited by the magnitude of the response. The sensor response has a maximum response of 2128 Hz shift for ~ 10 ppm DMMP; but at sub part-per-million levels, the response is erratic and extremely small. Thus, ECEL could be used as a coating to tell there is a high concentration of the

organophosphorus compounds; but low levels would go undetected, and the lower detection limits are needed for the chemical agents of which these compounds are simulants. Detection levels in the low part-per-billion range or less are the ultimate goal of these devices.

The PEM coating also is of limited use as a sensor coating for organophosphorus compounds because its response to low part-per-million and part-per-billion concentrations is very small. It is a better coating than either the ECEL or PVP coatings; but, PEM is not as good as the FPOL coating. PEM's response roughly scales as a function of the molecular weight of the vapor; but the response is more a function of the solubility of the vapor in the coating.

The FPOL coating is the best coating tested for use in detecting organophosphorus compounds. The response is an order of magnitude greater than the response obtained for PEM, and the response roughly scales as a function of the molecular weight. The response of the FPOL coating to sub part-per-million concentrations of DEEP vapor shows the use of the coating. It is disturbing to note the low response of the FPOL coating to the sub part-per-million concentrations of the DMMP vapor. This low response may be attributed to the error associated with the method of generating the vapor, a problem we learned to overcome. The GC analysis of the bubblers was of no use for the sub part-per-million levels of the vapors because the bubbler concentrations were below the limit of detection of the GC for the compounds. Because the purpose of the SAW work is really to detect the chemical agents, the analysis of sub part-per-million levels needs to be performed in even greater detail.

The SAW device does indeed show promise for use in detecting organophosphorus compounds; but, the choice of coatings is of paramount importance. The responses of the coatings tested range from no response at all for the PVP to a very large response for the FPOL. Even though the responses of the coatings are roughly a function of the molecular weight of the species, the solubility of the compound in the coating plays a much more important role in the sensor response. All of the compounds tested have the same general form R_2POR' . The R' and R groups vary in geometry, and this change in geometry of the molecule must be accounted for in designing the sensor coatings. The compounds tested were chosen as simulants for the chemical agents; but, the response of the sensors may not follow the trends noted for these simulants. The agents are organophosphorus compounds, and their geometries are vastly different than the simulants.